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Membrane filtration and extraction of biomolecules (polyphenols) from process water in thermomechanical pulp mills

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DISSERTAÇÃO DE MESTRADO APRESENTADA
À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO EM
ENGENHARIA QUÍMICA

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Abstract

Papermaking is an important industrial sector that generates a huge amount of waste, regardless of the manufacturing process. One of the processes to make pulp and paper is the thermo mechanical process. This process generates waste streams rich in substances of high value which may be used in other industries can be obtained. Among these substances, stand out polyphenols. These biomolecules may have applications in the fields of agro-food and pharmaceutical industries. Membrane filtration has the potential to be used to recover polyphenols from wastewater coming from thermo mechanical process of paper mill.

In this study, was done an optimization of the best operating conditions in the ultrafiltration of an effluent, to concentrate polyphenols. First two membranes, with the same cut-off but different material, was used to study the effect of operating conditions on the permeation flux and the retention of polyphenols. After was carry out the study of the best conditions to work with another membrane, with a smaller cut-off. After, fractionation of the effluent with the previously optimized operating conditions was conducted.

To the fractionation, was used a membrane with a cut-off of 10 kDa, made by cellulose acetate and a membrane with a cut-off of 1 kDa, made by polyethersulfone (PES). The membrane with higher cut-off was used to concentrate molecules with a molecular weight higher than 10000 $g.mol^{-1}$, and the 1 kDa membrane was used to concentrate the polyphenols.

Key words : polyphenols, Thermo Mechanical Process, ultrafiltration, cellulose acetate, PES, fractionation

Declaration

Declare, on oath, that this work is original and that all non-original contributions were properly referenced with identification of the source.

Índex

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Notation and Glossary

A	Membrane area	m^2
C	Mohr's salt concentration	$mol.L^{-1}$
C_f	Polyphenols concentration in feed	$mg.L^{-1}$
C_p	Polyphenols concentration in permeat	$mg.L^{-1}$
J	Permeation flux	$L.m^{-2}.h^{-1}$
M_f	Filter mass	g
M_i	Filter mass	g
P_f	Feed pressure	bar
P_p	Permeat pressure	bar
P_r	Retentat pressure	bar
Q	Permeate flowrate	$mL.min^{-1}$
V	Efluente volume	L
V_0	Volume sample	mL
V_f	Volume of feed	mL
V_r	Volume of retentat	mL
V_s	Volume spent in titration	mL
V_w	Volume of salt	mL

List of Acronyms

COD	Chemical Oxygen Demand
CNRS	Centre Nacional de la Recherche Scientifique
IPHC	Hubert Curien Multidisciplinar Institute
kDa	Dalton
MF	Microfiltration
MW	Molecular Weight
NF	Nanofiltration
NTU	Nephelometric Turbidity Unit
OMW	Olive Mill Wastewater
PES	Polyethersulfone
RePSeM	Laboratory of recognition and molecular separation processes
RO	Reverse Osmosis
TFF	Tangencial Flow Filtration
TMP	Thermo Mechanical Process
TMP	Transmembrane Pressure
UF	Ultrafiltration
VRF	Volume Reduction Factor
VW	Vegetation Waters

1 Introduction

1.1 Project Presentation

Papermaking is an important industrial sector and ever more the paper manufacturers have sought to cut their production costs by engaging in a process of sustainable development. In fact, the reduction of water consumption and the search for new ways to recycle their waste streams and waste could be solutions to increase their competitiveness.

Among the various methods of manufacturing pulp, the Thermo Mechanical method, TMP, comprises contacting wood chips with water at an elevated temperature. This method of production of high yield requires no chemical manipulation of matter and so is respectful of the environment. Are many effluents from this process, but these have the advantage of being rich in extractive that may have applications in the fields of agro-food and pharmaceutical industries [1].

Membrane filtration is one of the best choices for the extraction of this substances. It is toxic solvent free, provides easy automation and scale up, shorter process time, lower labour and energy costs, less waste disposal, and mild operation conditions. However, the membrane fouling in filtration is the main disadvantage which results in the decline of permeate flux. Usually the fouling is caused by deposition and accumulation of solute or colloidal particles at the membrane surface or inside the pores [2].

The main objective of this study is the isolation of polyphenols with high molecular weight coming from a TMP effluent in order to be used as an initiating agent for ‘polymerization’ and ‘condensation’ reactions to produce pitch. It is a bituminous substance manufactured from a specially selected feedstock, that can be a precursor in the production of high cost carbon materials.

To achieve a separation of these compounds by ultrafiltration, were first studied the optimum conditions for the use of a pre-treatment to the effluent. A method of optimizing the ultrafiltration was then carried out by studying the effect of operating conditions on the permeation flux and the retention of polyphenols. It was also considered the comparison of two membranes with the same cut-off but different materials to an evaluation of the best membrane, for a fractionation of the effluent.

1.2 Presentation of the host organization

1.2.1 The CNRS

The *Centre National de la Recherche Scientifique* (CNRS) is a public organization under the responsibility of the French Ministry of Higher Education and Research. Founded in 1939 by governmental decree, the CNRS's missions are evaluate and carry out all research capable of advancing knowledge and bringing social, cultural, and economic benefits for society, contribute to the application and promotion of research results, develop scientific information, support research training and participate in the analysis of the national and international scientific climate and its potential for evolution in order to develop a national policy [3].

With nearly 34 000 people (25 300 are permanent employees - 11,300 researchers and 14,000 engineers, technicians and administrative), a budget of 3.415 billion euros, of which 802 million of own resources, for 2013, a location on the throughout the national territory, CNRS operates in all fields of knowledge, based on more than 1,100 research units and services. It is present in all major disciplines grouped into ten institutes, including three national and 19 regional delegations. CNRS have more than 1100 research units and service are nearly 94% in partnership with higher education and other French research organizations. A proof of significant scientific contribution it's that until the end of 2012, 4521 new patents were filed, have 891 active licenses, and since 2000 were created 704 new companies.

The CNRS annually hosts approximately 4,600 foreign researchers, and 1690 become permanent employees. It has around 40 cooperation agreements with thirty countries, 293 international scientific cooperation programs, 158 international laboratories and 105 international research groups associated, and 30 international joint units. Also has permanent representations in Brussels, Hanoi, Malta, Moscow, New Delhi, Beijing, Pretoria, Rio de Janeiro, Tokyo and Washington [4].

1.2.2 Hubert Curien Multidisciplinary Institute (IPHC)

The Hubert Curien Multidisciplinary Institute was created in 2006 and is a combination of three departments: Department of Ecology, Physiology and Ethology, Department of Subatomic Research and Department of Analytical Sciences. Between 2006 and 2010, the institute has produced over 1,100 publications and 280 communications processes, and in 2011 the number of associated persons was 392, of which 266 are permanent employees [5].

1.2.3 The Laboratory of recognition and molecular separation processes (RePSeM)

This lab is attached to the Department of Analytical Sciences, and consists of a team of researchers and teachers, led by Prof. Barbara Ernst. Her work focuses on physical and chemical areas and separation sciences. This is a laboratory with various collaborations, in a national and international level.

1.3 Organization of Thesis

This thesis consists of six chapters.

Chapter 1 presents a short introduction, explaining the work and the objectives of this study, as well the presentation of the hot organization. Followed by chapter 2, that provides literature review of thermo mechanical process, of polyphenols in our work case and membrane separation.

The chapter 3 describes the detailed information and the characterization of all the materials used in this study as well as the equipment and the analytical methods.

The chapter 4 presents the characterization of the effluent.

Chapter 5 describes all the work made with membranes. First it's explained the process of fractionation and the respective results are presented. It's shown the results of the optimization of the pretreatment, as well as the optimization of the operating conditions of the membranes. Are also explained the effects of fouling and cleaning in this work.

In chapter 6 is described the conclusions of all the work that was made.

2 Literature Review

2.1 Paper Industry – TMP

Today, a shift away from a fossil-based resource economy towards a bio-based resource economy is desirable. In this type of economy, plant biomass, such as wood and straw, would be used as the primary source for producing energy and materials. At the same time, the production of high added value products within a wood bio refinery concept would offer new opportunities for pulp and paper and forest resources industries wishing to diversify their products and thus become major players in "Green Growth". The extraction and recovery of by-products of wood during chemical pulping is now an economic model and universally employed. But, to our knowledge, the recovery of potential high value compounds has not been explored in the field of Thermo-Mechanical Pulping (TMP). In Thermomechanical pulping, TMP, pulp is made by heating the chips with steam and mechanically separating the fibers in a pressurized refiner (Figure 1).

The early stages of TMP in the pulp and paper industry can be regarded as a process of solid-liquid extraction for different extractives (dissolved and colloidal substances) that are transferred in aqueous phase. The high-yielding production of TMP allows to consider a high release of wood extractives into the effluents and the available flow rates range from 700 $m^3.d^{-1}$ to 2500 $m^3.d^{-1}$. Furthermore, TMP provides an advantage in terms of the quality of molecules recovered ("Green" label) without using chemical product [6].

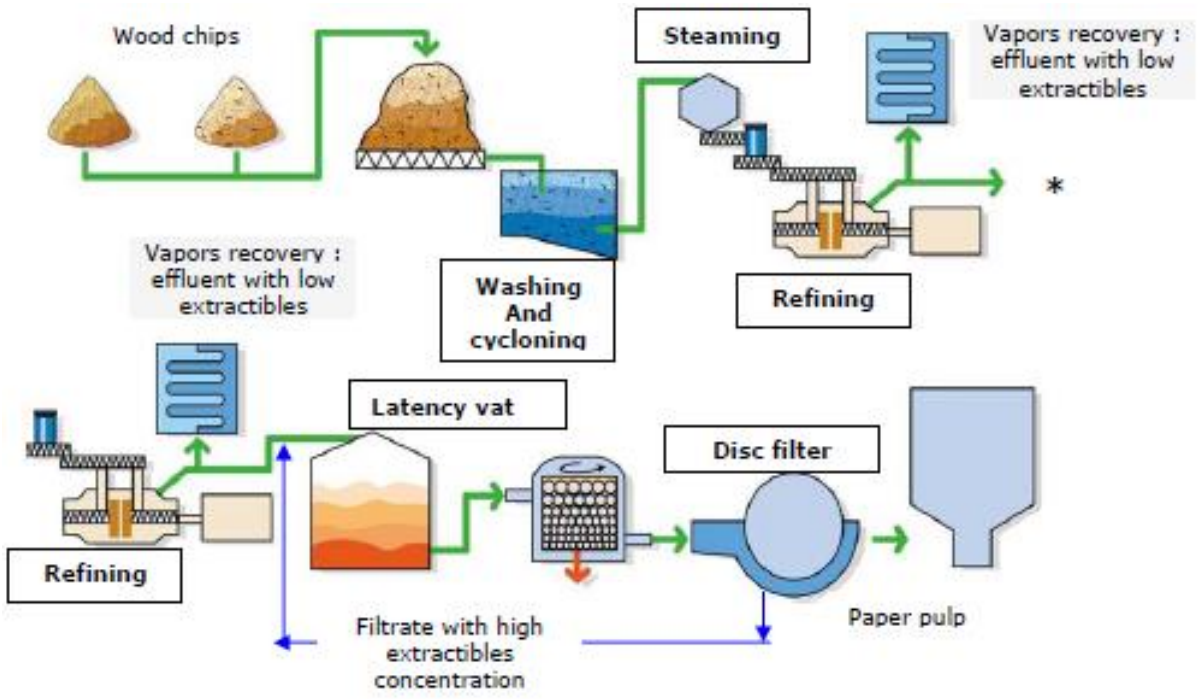


Figure 1: Thermomechanical pulping system [6]

In the Figure 1, the main line describes the paper pulp circuit which starts with the wood chips and end with the silo. Different effluents are generated along the circuit and several can be considered as interesting for the release of extractives: effluents coming from the latency vat and from the disc filter (commonly called the “clear filtrates”) and the refining (commonly called the “press filtrates”). These last one were the object of the study.

2.2 Biomolecules and wood extractives

2.2.1 Biomolecules and wood extractives in TMP effluent

The substances which are released with the TMP, are cellulose, Hemicelluloses, lignin and extractives. Table 1 shows the difference between the chemical composition of softwoods (coniferous woods that belong to the group of gymnosperms) and hardwoods (broadleaf woods belong to the group of dicotyledonous angiosperms).

Table 1: Average % Chemical Composition of softwoods and hardwoods [7]

Constituent	Softwoods	Hardwoods
Cellulose	42 ± 2	45 ± 2
Hemicellulose	27 ± 2	30 ± 5
Lignin	28 ± 3	20 ± 4
Extractives	3 ± 2	5 ± 3

Cellulose is a macromolecule formed linearly chained cycles, that is to say about 500 to 5000 glucose monomers connected to each other by glycosidic linkages β -1,4-units. Different channels, side by side, are linked by numerous hydrogen bonds that give at this material a very high rigidity and explain that it is the substance of support of young plant cells [8]. In Figure 2 is represented schematically the connection between glucose monomers.

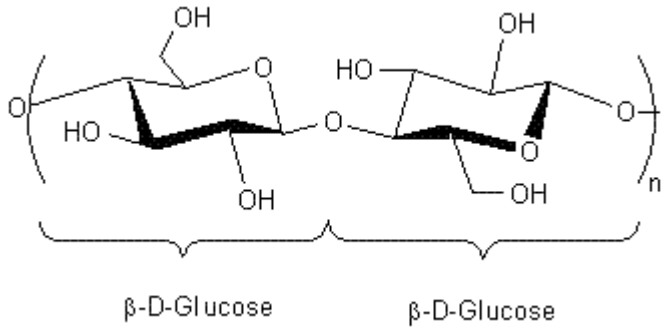


Figure 2: Glycosidic Linkages [8]

Hemicelluloses are polymers of shorter or branched formed from pentoses (sugars with five carbon atoms such as xylose), or hexoses other than glucose (for example, galactose). Whatever kind of tree, we find the same structure for cellulose while hemicelluloses have compositions and structures that they vary considerably from hardwood or softwood. Xylans such as found in abundance in birch (*Betula pendula* and *Betula lenta*) correspond to units of the xylopyrannose united together by links β -1 -> 4-glycoside. In xylans there also has lateral substituents glucuronic acid and alcohol groups (-OH) are methoxylated (converted into-OCH3), and Glucomannan or galactomannan exist in greater quantity in softwood. [8]. In Figure 3 is represented schematically the methoxylation of alcohol in the hemicellulose molecule.

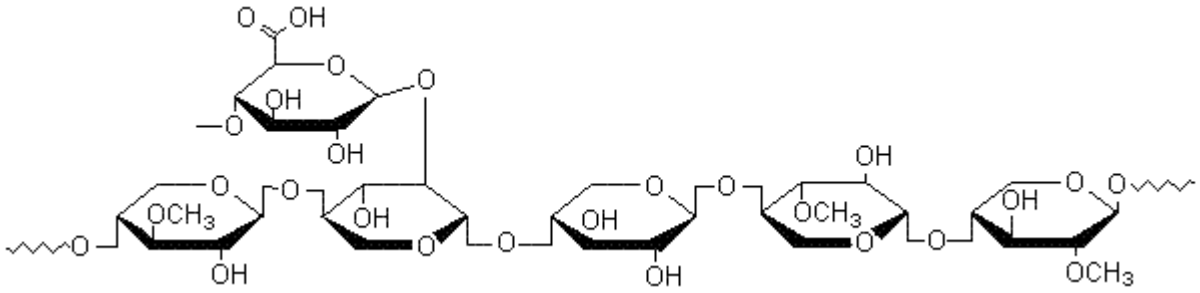


Figure 3: Methoxylation of alcohol [8]

The lignin is the third component of the cell wall (the secondary component of plant cell walls). It's a cross-linked polymer (three-dimensional) and the complex structure varies, as hemicelluloses, depending on the species, age of the plant and climatic conditions [8]. The macromolecule is synthesized by radical via from three p-hydroxy-cinamyl precursor alcohols: p-cumaryl, coniferyl and sinapyl. Depending on the degree of methoxylation of the aromatic ring, it is said that the basic unit is p-hydroxyphenyl (not methoxylated derived from p-cumaryl alcohol), guaiacyl (having a methoxyl, derived from coniferyl alcohol) and syringyl (two methoxy groups derived from the alcohol sinapyl). While lignins of coniferous woods are composed almost exclusively of guaiacyl units, called G-type of lignins, lignins from hardwood timbers are richer in syringyl units, termed type GS lignins [9].

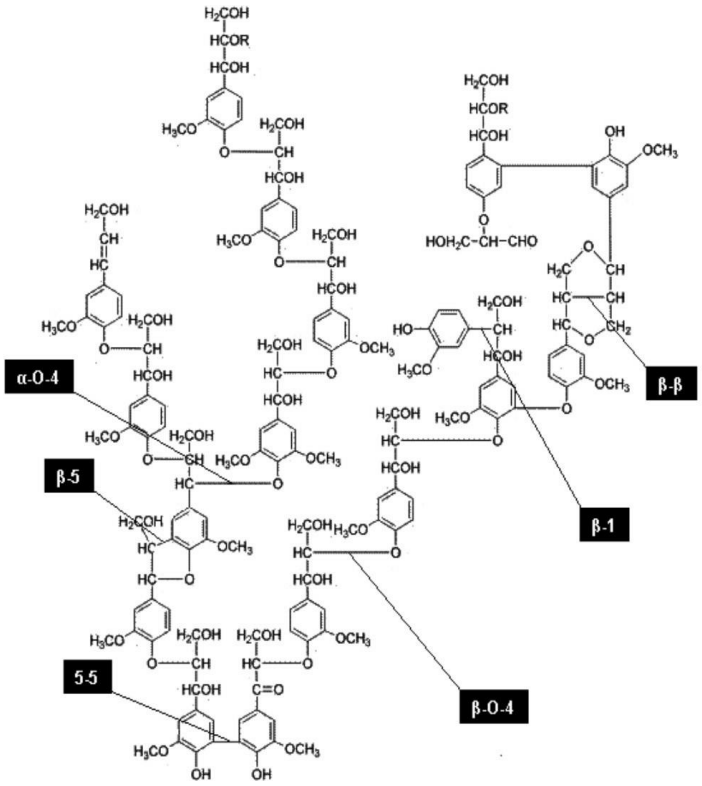


Figure 4: Main types of links between the basic units that make up lignin (lignin type G). [9]

The extractives are low molecular weight compounds present in the porous structure of the wood. Their name derives from the fact that they can easily be extracted with organic solvents or water. In effect, they are not bound to the cell wall structure by covalent bonds and thus are solvent accessible. Extractives give to wood specific characteristics such as color, odor, durability, as well as mechanical and acoustic properties. These components are often classified as secondary metabolites, i.e a product of plant metabolism that are not essential for growth, in contrast to primary metabolites, such as proteins and carbohydrates [7].

The extractives content may vary taking into account various natural factors, such as gender and tree species, geographical origin (continent, country) or part of the wood in question (trunk, branches), and increases gradually from the heart to the periphery. The extractable are constituted by the families of the following organic compounds: polyphenols, terpenes and terpenoids, waxes and fats, complex carbohydrates and nitrogenous compounds.

Polyphenols and terpenes are the most abundant extractable compounds. They have interesting practical applications in food, pharmaceutical and cosmetic area [7].

Terpenes (isoprenoids or terpenoids) form a subclass of prenyl lipids (terpenes, prenilquinonas, and sterols), representing the oldest product group of small molecules

synthesized by plants. Terpenoids may be described as modified terpenes which methyl groups are rearranged or removed, or oxygen atoms, oxidized are added.

The terpene hydrocarbons are defined as a group of molecules whose structure is based on a defined number of isoprene units (methyl-buta-1 ,3-diene) with the formula C_5H_8 (Figure 5). Are often found in essential oils from plants and contains the quintessence, the fragrance of plants. [10].

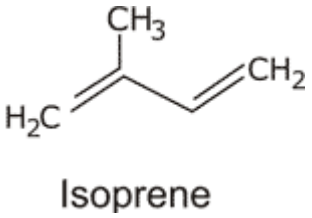


Figure 5: Structural formula of isoprene (methyl-buta-1, 3-diene) [10]

Due to their biological activity, terpene extractives have always aroused great interest in the pharmaceutical field. Studies have shown that these biomolecules possessed effective anticancer activity, in particular in the treatment of breast, ovarian and prostate cancer. The diterpene paclitaxel, with a commercial name Taxol, is an example. Some terpenoids, such as carotenoids and phyrol, are essential for plant physiology [7]. In nature there are more than 1000 monoterpenes, 7000 sesquiterpenes and 3000 diterpenes [10].

Polyphenols include a wide range of more than 8000 compounds [7]. The importance of polyphenols is due to their positive contribution to cellular processes within the body. In terms of pharmacological activity, they protect against the oxidation of high-density lipids (HDLs). They help the body to retain important HDLs while helping to remove problematic low-density lipids (LDLs). Additionally, polyphenols also have anti-ulcer, anti-carcinogenic and anti-mutagenic activities. The reason for these activities is the strong antioxidant nature of polyphenols, which is based on their ability to absorb free radicals. Polyphenols are broadly distributed in the plant kingdom and are the most abundant secondary metabolites found in plants, and they include many classes of compounds ranging from phenolic acids, colored anthocyanins, and simple and complex flavonoids [11].

Polyphenols of vegetable kingdom, which have been studied, are numerous. For example, gallic acid is mainly used as a standard, the (-)-epicatechin is the stereoisomer of the most abundant catechins in tea leaves, ferulic acid participates in the synthesis of lignin, which forms the walls of the plant cells and is a precursor of the aromatic acid molecules, syringic acid, that can be found in large quantities in the skin of grapes, plays a role in alcoholic fermentation, and the vanilique acid is part of the business of the vanilla aroma [7].

2.2.2 Structure of polyphenols

Oligomeric proanthocyanidins (OPCs) are a class of polyphenolic biflavanoids that are found in high concentration in grape seeds, tea leaves and pine tree bark. Their importance as powerful antioxidants is significant to biological beings because they have been tested as being more effective than vitamins C, E, and b-carotene. They consist of proanthocyanidin subunits referred to as monomers. Oligomeric proanthocyanidins are made up of two or more monomers that are chemically bonded. Catechin and epicatechin are the two proanthocyanidin monomers. The structures of catechins (monomers) and some procyanidins are shown in Figure 6. Dimers, trimers, tetramers, and so on are created when each of these two monomers bind at the alpha or beta position on their molecular structures. In addition, catechin and epicatechin can combine to create esters such as catechin/epicatechin gallate. They can also bond with sugars and proteins to create glycosides and polyphenolic proteins. About 162 dimers, including gallic acid and glucose esters, can be created [12].

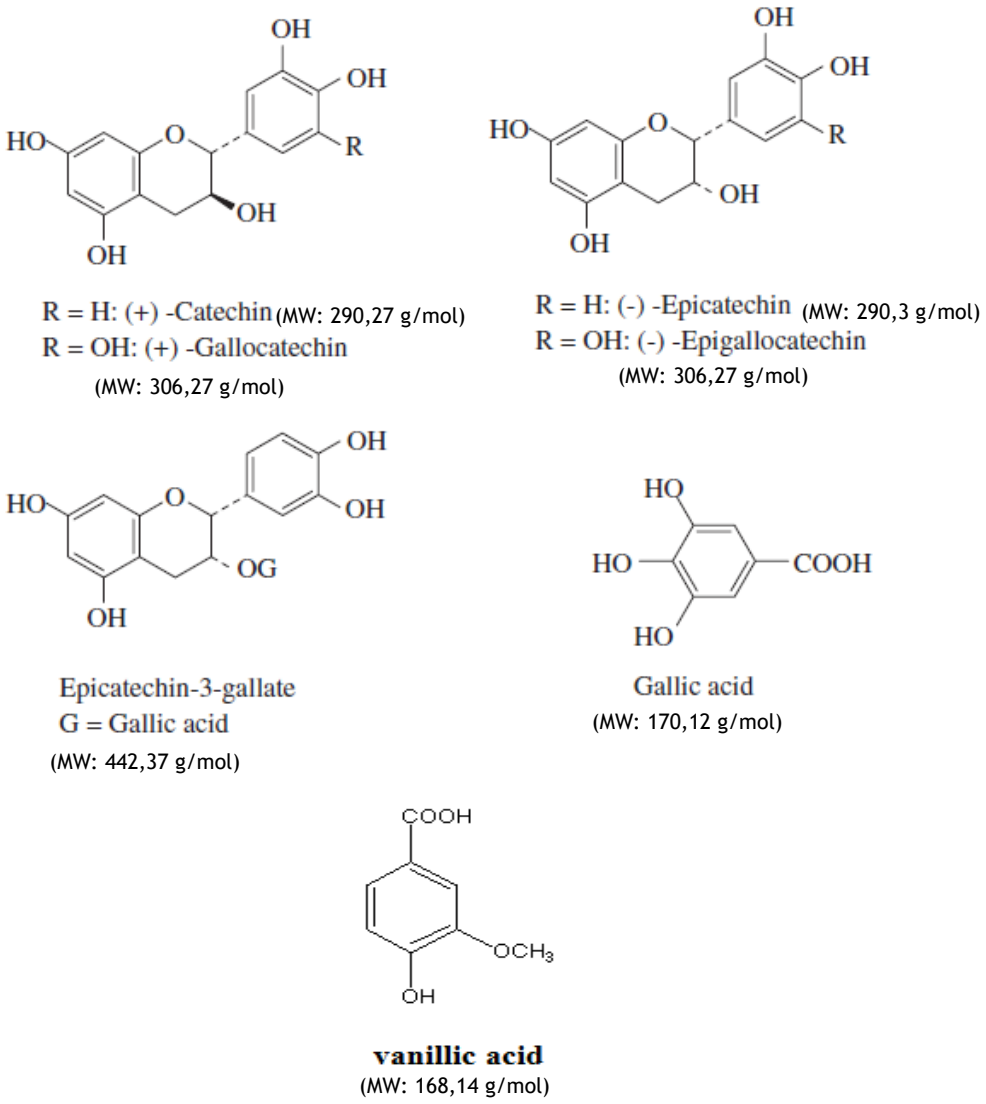


Figure 6: Structures of major polyphenols that can be found in pine tree bark [11]

The process leading to the production of polymers (esters) from monomers is called polycondensation. During this process, there is the elimination of by-products of low molecular weight (for example, water, alcohols, halides and hydrogen). Polycondensation is often complicated by side reactions, in which both the original monomers and the polycondensation products (oligomers and polymers) may participate. Such reactions include the reaction of monomer or oligomer with a mono-functional compound (which may be present as an impurity), intramolecular cyclization (ring closure), and degradation of the macromolecules of the resultant polymer. The rate competition of polycondensation and the side reactions determines the molecular weight, yield, and molecular weight distribution of the polycondensation polymer. This reaction is characterized by the disappearance of the monomer in the early stages of the process and a sharp increase in molecular weight [13].

Polycondensation processes play an important role in nature. Polycondensation or similar reactions are the basis for the biosynthesis of the most important biopolymers— proteins, nucleic acids, and cellulose [13]. An example of polycondensation which has been studied over the years is the formation of humus. Several pathways exist for the formation of humic substances during the decay of plant and animal remains in soil. The classical theory is that humic substances represent modified lignins, but the majority of present-day investigators favor a mechanism involving quinones or a sugar-amine condensation. A lignin pathway may predominate in poorly drained soils and wet sediments (swamps, etc.) whereas synthesis from polyphenols may be of considerable importance in certain forest soils. The frequent and sharp fluctuations in temperature, moisture and irradiation in terrestrial surface soils under a harsh continental climate may favor humus synthesis by sugar-amine condensation [14].

The pathway that involves polyphenols can occur in two ways. In the first way, phenolic aldehydes and acids released from lignin during microbiological attack undergo enzymatic conversion to quinones, which polymerize in the presence or absence of amino compounds to form humiclike macromolecules (Figure 7 (1)). The other way is somewhat similar except that the polyphenols are synthesized by microorganisms from nonlignin C sources (e.g., celulose) (Figure 7 (2)). The polyphenols are then enzymatically oxidized to quinones and converted to humic substances. Possible sources of phenols for humus synthesis include lignin, microorganisms, uncombined phenols in plants and tannins [14].

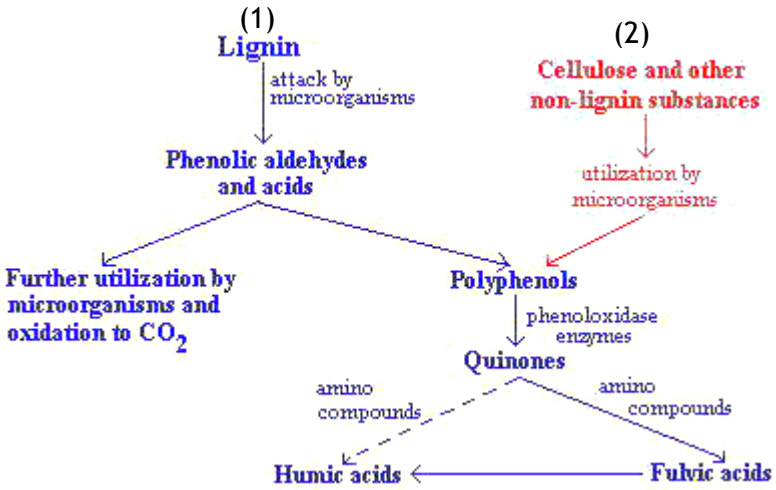


Figure 7: The polyphenols pathway of húmus formation [14]

Today, one main challenge for petroleum refiners/petrochemical producers is the effective utilization of petroleum residues produced during various petroleum refinery/petrochemical processes. Generally, these residues are used as blending streams for fuel oils but the market of fuel oil is shrinking. To fetch substantial money out of these low value petroleum residues, one way is to convert these petroleum residues into pitch. Pitch is a widely used precursor for making many low volume but high cost 'industrial' and 'advanced' carbon materials [15]. In this context, a petroleum refiner would like to evaluate the capacity of nature polyphenols coming from wood to be used as an initiating agent for 'polymerization' and 'condensation' reactions to produce pitch.

2.3 Membrane Separation

2.3.1 Generality about the membrane separation

Membrane technologies have been shown to provide solutions to the operations of separation, fractionation and recovery of valuable biomolecules.

There are many membrane processes, based on different separation principles or mechanisms and specific problems, can cover the broad size range from particles to molecules. The membrane is at the heart of every membrane process and can be considered as a permselective barrier. A schematic representation of membrane separation it's represented in Figure 8 [16].

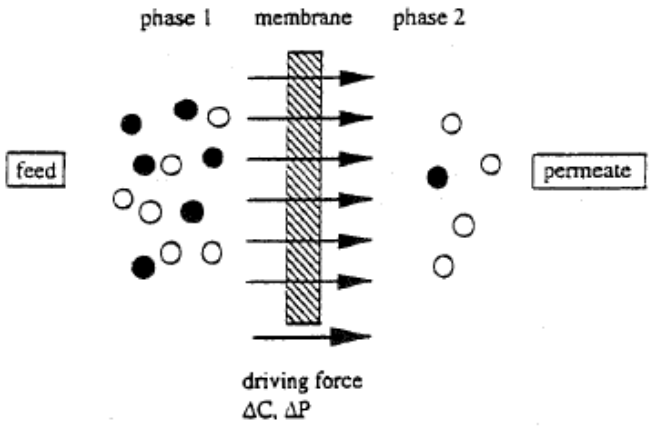


Figure 8: Schematic representation of a two-phase system separate by a membrane [17]

The main categories of membranes cover microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) with a pore size range from 2 µm to 0.5 nm, and reverse osmosis (RO). As seen through the Table 2, Reverse osmosis (RO) offers the finest degree of separation, followed by nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), which has the largest pore size [16].

Table 2: Comparisons of the four membrane processes [2]

Membrane Process	Pore diameter	Rejected Components	Operating Pressure	Applications
Microfiltration	4 – 0.02 µm	Bacterias, clay	<2 bar	Water and wastewater treatment, Sterilisation
Ultrafiltration	0.2 – 0.02 µm	Proteins, colloids, polymers	1 – 5 bar	Concentration of macromolecules, Enzyme recovery
Nanofiltration	<0.002 µm	Mono-, di- and oligosaccharides	5 – 20 bar	Fractionation of crude extracts, Water Softening
Reverse Osmosis	0.002 µm	Amino acids, glucose	10 – 100 bar	Sea water desalination

2.3.2 Fractionation of wood substances with membrane

The isolation of polyphenols with high molecular weight coming from a TMP effluent can be carried out with membrane technology. The petroleum refiner is particularly interesting by the compounds with a molecular weight in the range from 1000 to 10.000 $g.mol^{-1}$.

Russo [18] used a selective membrane fractionation to fractionate vegetation waters (VW) in three principal streams consisting in purified and enriched antioxidant polyphenols with low molecular weight (MW), pure vegetable water and a concentrate of organic substances without or extremely impoverished of the polyphenolic content. The VW was acidified, to prevent phenols oxidation, and then filtered in microfiltration using ceramic membranes of 0.8 and 0.45 μm and a polymeric spiral-wound membrane of 500 kDa. The permeate of MF was filtrated by ultrafiltration, using polymeric membranes of 80, 20 and 6 kDa, and the permeate of the last one was filtrated with a ceramic membrane of 1 kDa. The UF permeate was concentrated in reverse osmosis. MF holds all the suspended solids and shows a rejection of total nitrogen and sugars of 40% and of minerals of 25%, and the concentration of polyphenols increase about 84%. In UF, the 6 and 1 kDa membranes show the same selectivity in respect of polyphenols and differ only for the rejection values. The 6 kDa membrane rejects 45% of polyphenols (mainly hydrotyrosol), and the 1 kDa, used in the permeate of 6 kDa, rejects more 31%. RO concentrates all the components present on the UF permeate.

Paraskeva *et al* [19] applied a membrane filtration technology for the treatment of olive mill wastewater (OMW). Ultrafiltration, nanofiltration and reverse osmosis techniques were applied for the system, in order to study and optimize the fractionation procedure. The process water was pre-filtered with an 80 μm polypropylene screen, and then filtered with a UF membrane made of ceramic material (zirconia) with an area of 0.24 m^2, and with a operating temperature of 15 – 35 ºC and a TMP between 1.0 and 2.25 bar. The permeate from the UF unit was used to feed the NF or RO membranes. Polymeric membranes in spiral wound were used for either NF (cut-off of 200 Da) or RO (cut-off of 100 Da) tests, with an active area of 2.5 m^2. Typical TMP values used in NF are in the range of 10-30 bar, whereas for RO, TMP values are in the range of 30-40 atm. Better performance of UF unit may be obtained at higher temperatures (50ºC) and TMP values between 1.50 and 1.75 bar. With these operating conditions there is retention of solids up to 90% and a concentration of phenolic compounds of about 50%. In NF, the temperature was kept constant at 20ºC and the pressure that gave better results was 20 bar. The major part of organic compounds remained in the concentrate streams, and the rejection was about 71%. In RO, the temperature was kept constant at 35ºC and a TMP of 40 bar. The phenols and other organic compounds remained in the concentrate stream, and the rejection was about 98.95%.

Persson *et al* [20] used a process in which the separation of substances in the TMP process effluent was achieved by filtration and membrane filtration only. Drum filtration (DF) is used in the first stage to remove particles and fines. Extractives and remaining suspended solids in the filtrate are removed in the second stage by microfiltration (ceramic membrane, inner diameter about 0.2 µm). Hemicelluloses are concentrated by ultrafiltration (polyethersulfone membranes, MWCO = 5 kDa) in the third stage, and, finally, the UF permeate, containing sugar, lignin and salt, is purified by nanofiltration. For each ton of pulp produced, about 10 kg of suspended matter, more than 0.3 kg of extractives, 11 kg of hemicelluloses and 8 kg of aromatic compounds could be recovered. About 40% of the treated process water could be recovered as fresh water. The aim of this work was to study the fractionation of process water coming from TMP (Figure 9).

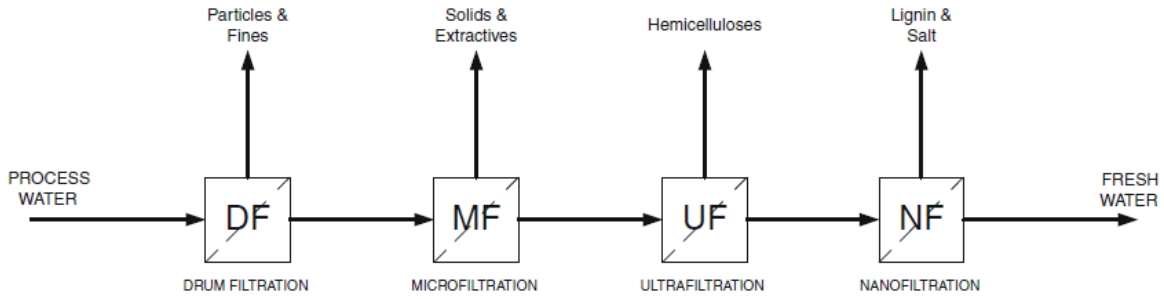


Figure 9: A schematic illustration of the overall process [20]

3 Materials and Methods

3.1 TMP Circuit

The effluent used in this study comes from the Norske Skog paper industry.

3.1.1 Clear Filtrate

At the end of the process, filtering is performed for thickening the pulp and filtrate is recovered to the upstream process steps. These procedural waters contain removable and colloidal substances.

3.1.2 Press Filtrate

During TMP circuit, the fibers are gradually hydrated. After washing, the wood chips are pressed, which allows the extraction of substances, which means that these process waters containing large amounts of resin acids, polyphenolic acids, carbohydrates and lignins.

3.2 Analitycal Techniques

3.2.1 Chemical Oxygen Demand

COD is a measure for assessing the degree of pollution by oxidizable materials by measuring the amount of oxygen required to chemically oxidize.

The sample is added to a reagent mixture consisting of potassium dichromate in known amount, of concentrated sulfuric acid with silver sulfate and mercury sulfate, and is boiled to 150ºC at reflux for 1:30h. The silver sulfate is a catalyst oxidation of long-chain organic compounds. Mercury sulfate is used to complete the chloride ions to prevent their oxidation. The remaining excess dichromate is reduced by a standard solution of iron II sulfate and ammonium (Mohr's salt).COD is the concentration in mg $O_2.L^{-1}$ equivalent to the amount of dichromate consumed by dissolved solids.

The COD value may be calculated by the following equation:

$$COD = \frac{8000 * C * (V_w - V_s)}{V_0} \qquad 3.1$$

In this equation, C is the concentration of Mohr's salt, in $mol.L^{-1}$, V_0 represents the volume of sample used, which is 10 ml, V_w is the volume of Mohr's salt spent in the water titration, and V_s represents the volume spent in sample titration, in mL.

The effluent sample was previously diluted with a dilution factor of 10. The device used is the digest Automat K-438 Büchi automatic digestion system.

3.2.2 pH

The determination of pH was performed with microprocessor pH meter pH211 by Hanna Instruments. Before each use, the calibration was performed with standard solutions of pH 4, 7 and 10.

3.2.3 Turbidity

The device used is TurbiDirect Lovibond and the unit of measurement is the Nephelometric Turbidity Unit (NTU). The calibration of the device is checked before each use, using standard solutions of known turbidity (<0.1, 20, 200, 800 NTU).

3.2.4 Suspended matter and dry matter

The amount of organic and inorganic suspended solids in the water is measured by suspended solids. To check the suspended matter, a known volume of effluent is filtered using a vacuum pump on fiberglass filters of diameter 0.45 microns.

First, the filters are weighed, and after filtration has occurred are placed in a moisture analyzer MB35, at 105ºC, and then weighed again. Using the following equation it is possible to calculate the concentration of suspended matter, in $g.L^{-1}$:

$$Suspended\ Matter = \frac{M_f - M_i}{V} \qquad 3.2$$

In this equation, M_f and M_i represents the final and initial mass of the filter, in grams, respectively and V represents the volume of effluent filtered, in liters.

The measurement of dry matter includes both suspended solids and dissolved solids (dissolved organic matter and mineral salts). In this case, 50 mL of effluent are introduced into a metal capsule, previously weighed, and then put in the oven at 105ºC, during 24h. Then the metal capsule it's weighed again and the difference of the final and initial weight represent the weight of the dry residue.

3.2.5 Determination of concentration of polyphenols

Total polyphenolic content was determined with the Folin-Ciocalteu method. In this method, the reagent is an acid green in color compound by phosphotungstic acid and by phosphomolybdic acid, oxidizes phenolic compounds, being reduced to a mixture of blue oxides of tungsten and molybdenum [1].

5 mL of Folin-Ciocalteu reagent, diluted 10 times, was added to 1 mL of sample and 4 mL of sodium carbonate, with a concentration of 75 $g.L^{-1}$. The mixture was then put in a water bath

at 50ºC for 5 min and between 5 and 10 min at room temperature, to cool. It can also be put into cold water for cooling it faster. After, the absorbance of the mixture was read at 760 nm. The absorbance measured is proportional to the amount of oxidized phenolic compounds, and this relation is represented by the Beer-Lambert law. A calibration curve was done with a solution of gallic acid [21].

For determining the absorbance, the UV-2401 PC was used, a UV-VIS recording spectrophotometer by Shimadzu.

3.3 Pretreatments

The configuration of the filtration (Cassette) module did not allow a direct use of the effluent. Colloids and suspended solids can clog the pores inside the cassette.

To optimize the filtration paper, two types of paper were tested: a chromatographic paper with 3 mm thick (hard paper) and a thinner paper with a weight of 0,014 kg / sheet (light paper), from Verlabo. In Figure 10, it's shown the equipment used in the pretreatment.

Figure 10: Filtration with paper [personal source]

Before and after each filtration, the turbidity, suspended matter and concentration of polyphenols were measured.

3.4 Ultrafiltration

3.4.1 Ultrafiltration membranes and set up

On this work were used three T-Series TFF Cassettes with Omega™ flat membranes. Two of them are made by polyethersulfone (PES), with cut-offs of 10 and 1 kDa, and one is made by cellulose acetate, with a cut-off of 10 kDa. The effective filtration area it's of 0.0186 m^2 for the three cassettes. The used experimental set-up (Tangential Flow Filtration system, TFF) which was supplied by Pall cooperation France is described in the Figure 11.

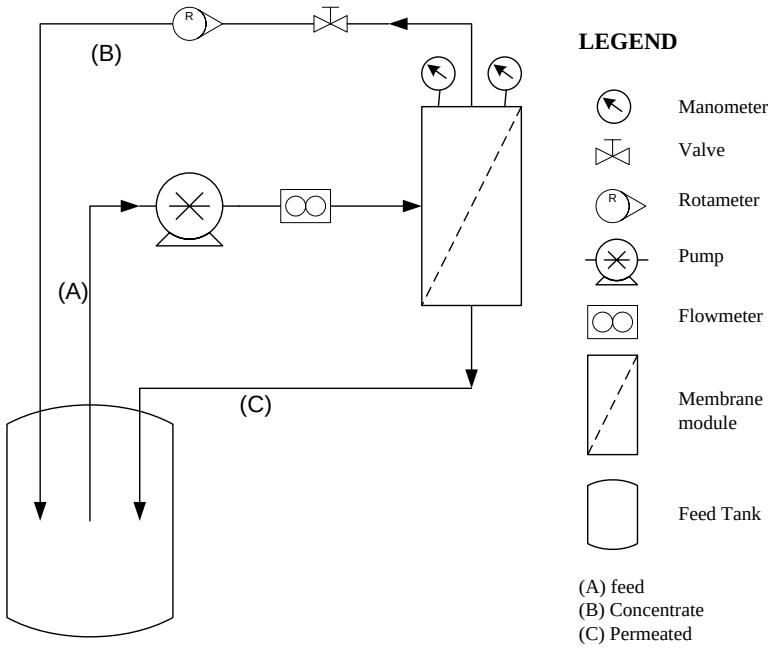


Figure 11: Schematic of ultrafiltration experimental units

It is exerted on the membrane a transmembrane pressure (TMP) in order to move the molecules through the filter. The fluid containing the substance retained is called retentate, while the fluid passing through the membrane is called permeate or filtrate. The temperature was maintained at 25°C for each experiment. During optimization of the operating conditions, the experiments were carried out at constant concentration (concentrate and permeate were circulated back to the storage tank). Then, the permeat was not re-circulated for the concentration mode.

Three recirculation fluxes were tested, for different values of TMP (1, 2 e 3 bars). In membranes with a cut-off of 10 kDa, recirculating flows of 0.6, 0.4 and 0.2 $L.min^{-1}$ were

used, and on the other membrane were used recirculation flows of 0.8 and 0.6 $L.min^{-1}$, whereas it was very difficult to perform passing the fluid through the membrane.

3.4.2 Permeability and water flux

The membrane permeability was measured using osmosed water. The flux values (J_0) were measured by applying different flow rates and transmembrane pressures. After each test with the effluent, the membrane was washed with water, and water flow (J_i) was measured under the same conditions as those of permeability. This flow of water, after washing, evaluates the irreversible clogging of the membrane. If J_i was lower than J_0, the membrane was cleaned with a 0.1M solution of sodium hydroxide.

4 Characteristics of waters coming from the Thermal Mechanical Process

The effluent comes from a part of the process where the chips are washed and pressed which causes that the colloidal nature of effluent is very high. The colloidal particles are stable with poor aggregation sensitivity that is due to a steric stabilization by wood polymer, e.g. polysaccharides and electrostatic stabilization by carboxyl and hydroxyl groups present on the surface. According to Puro et al, such colloidal particles are for instance lipophilic extractives, generally called as wood resin [22].

The characteristics of the effluent are shown in Table 3.

Table 3: Characteristics of the effluent

Effluent	Filtrate Press Raw
Color	Light brown
COD (mg O_2.L^{-1})	4275
pH	5.76
Turbidity (NTU)	610
Suspended Matter (g.L^{-1})	0.98
Dry Matter (g.L^{-1})	2.21
Total Polyphenols (mg.L^{-1})	289

The procedural waters have a light brown color, with a high turbidity. It contains a high concentration of dry matter in comparison to suspended matter. The COD value is quite high indicating the presence of a high concentration of dissolved oxidisable material.

Over time there was a decrease in turbidity of the effluent, as well as a decrease in MES (suspended matter) indicating that most of the turbidity is due to suspended matter. The amount of dry matter remained constant. There was a decrease in the COD value indicates that the oxidation of organic matter.

The total polyphenols concentration was about 289 mg.L^{-1} but during time was an increase of this value until a concentration of about 342 mg.L^{-1}. This increasing could be explained by the oxidation of some substances, which may lead to erroneous results.

5 Fractionation with Ultrafiltration membrane

Process water from the thermomechanical pulp mill was divided into four fractions by filtration and Ultrafiltration membranes. In the first stage, a paper filtration was used to remove particles and fines. Then, the permeate of this filtration was subject an ultrafiltration with 10 kDa and 1 kDa membranes successively in order to obtain 3 fractions as described in Figure 12 :

- compounds with a MW > 10000 $g.mol^{-1}$. In according to the Persson et al (2010) the High molecular weight substances such as hemicelluloses are concentrated with the 10 kDa membrane.
- compounds with 1000 $g.mol^{-1}$< MW < 10000 $g.mol^{-1}$. The target polyphenols (C_3 – C_6) could be concentrated with 1 kDa membrane.
- compounds with a MW < 1000 $g.mol^{-1}$

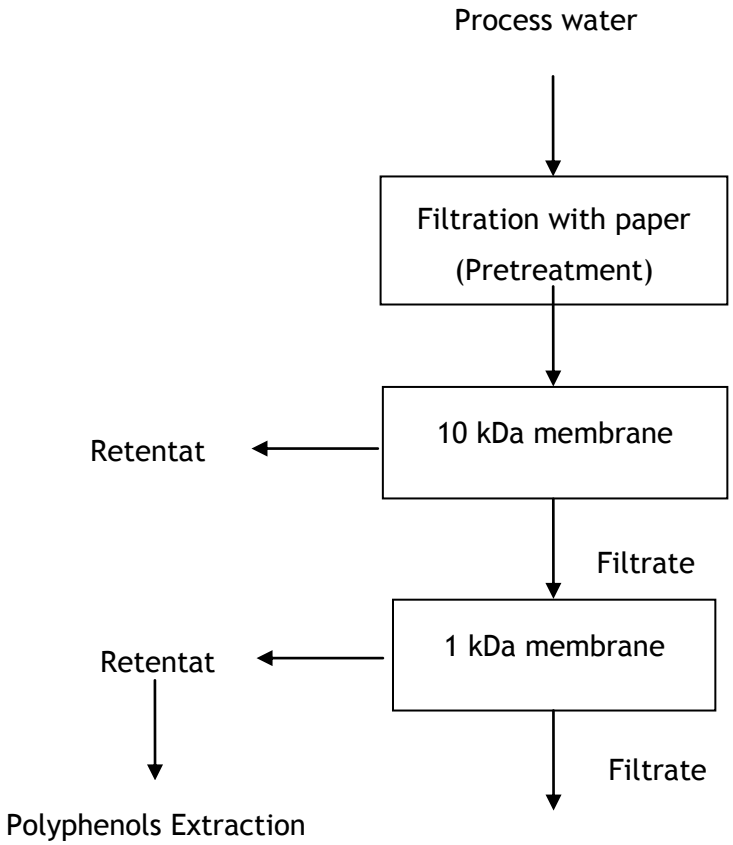


Figure 12: Schematic representation of the objective of this study [personal source]

5.1 Filtration

A coarse filtration was selected as a first stage (pretreatment) of the effluent in order to reduce the colloidal and fouling character of the effluent without a high loss of polyphenolic compounds.

First a normal filtration was performed with each type of paper. In this configuration, the results were unsatisfactory. With hard paper the removal of turbidity was about 32% and the removal of suspended matter was about 71%, and with light paper the removal of turbidity and suspended matter was 44% and 93%, respectively. Despite the removal of suspended matter is high, especially when the light paper was used, the removal of turbidity has a low value.

In an attempt to try to get better results, were performed filtrations with two filters together, both of the same paper. This configuration was made for two types of paper.

To obtain results for comparison with the already obtained, two successive filtrations were performed. The effluent was first filtered with hard paper, and the filtrate was filtered again with light paper. In a second attempt, the effluent was filtered twice with light paper.

The effectiveness of the pretreatment was measured according to the measurement of the turbidity, suspended matter and polyphenols concentration, before and after each filtration. In Figures 13 is represented the comparison between the two types of paper.

As seen in Figure, the best filtration method is to use both types of paper. Although both methods remove the same amount of suspended matter, turbidity removal is greater when the light paper is used for the both steps. However, the retention of polyphenols is smaller when the hard paper was used before the light paper. In this configuration of filtration, there was a reduction of turbidity of about 49%, a reduction of suspended matter of about 90% and only retention of polyphenols retention of 1.5%. In the work of *Persson et al* [20], it was used a drum filter in the pretreatment of the process water. In this study, the drum filter retained about 90% of the suspended matter, however, the retention of extractives was about 20% which is considerably high in view of these biomolecules are the target of study.

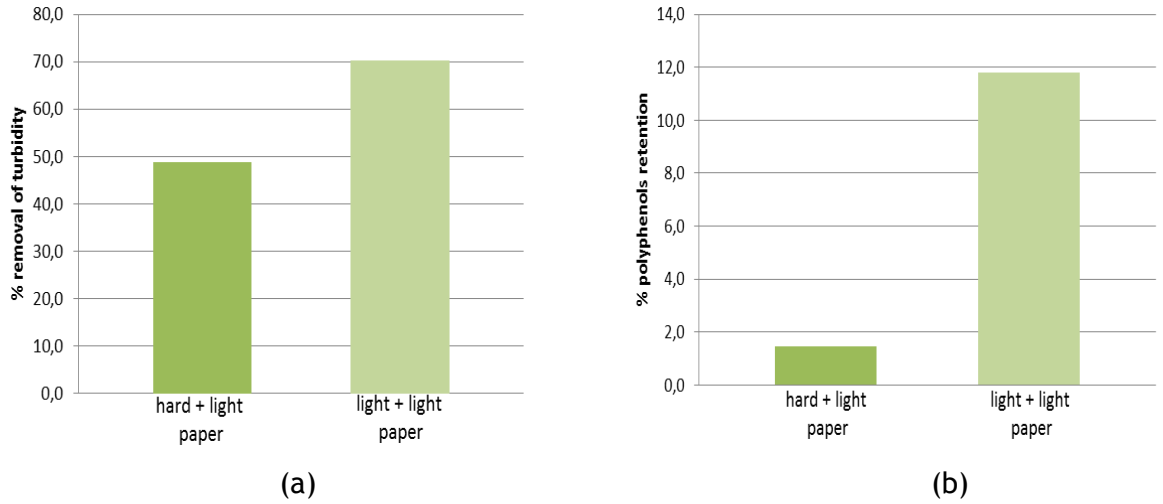


Figure 13: Comparison between the two types of paper. Graph (a) represents % of removal of turbidity and graph (b) represents the % of retention of polyphenols.

5.2 Fractionation with 10 kDa and 1 kDa membranes

The aim of this work was to optimize the performances of each of the ultrafiltration stages (10 KDa and 1 KDa). The operating conditions (transmembrane pressure and flowrate) and the membrane material were considered to provide better conditions for the fractionation of the effluent.

5.2.1 Optimization of operating conditions

The most important parameter in the membrane filtration processe is the permeate flux which is influenced by the transmembrane pressure (TMP) and cross-flow velocity or its equivalent feed flowrate. The permeate flux is defined in according the equation:

$$J = \frac{Q}{A} \qquad 5.1$$

In this equation, J represents the permeation flux, in $L.m^{-2}.h^{-1}$, Q represents the permeate flowrate, in $mL.min^{-1}$, and A it's the membrane surface area, in m^2.

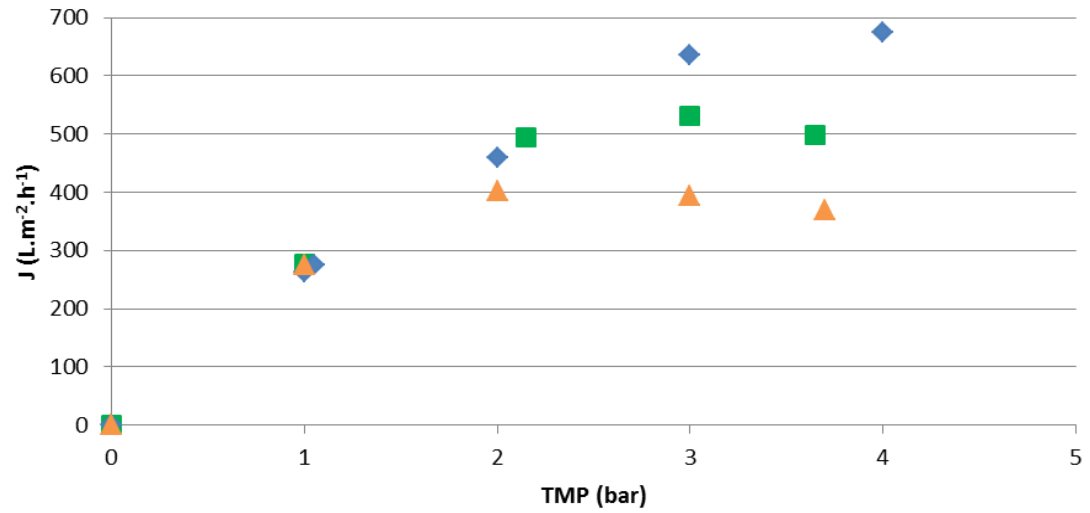
The transmembrane pressure can be calculated by the following equation,

$$TMP = \frac{P_f + P_r}{2} - P_p \qquad 5.2$$

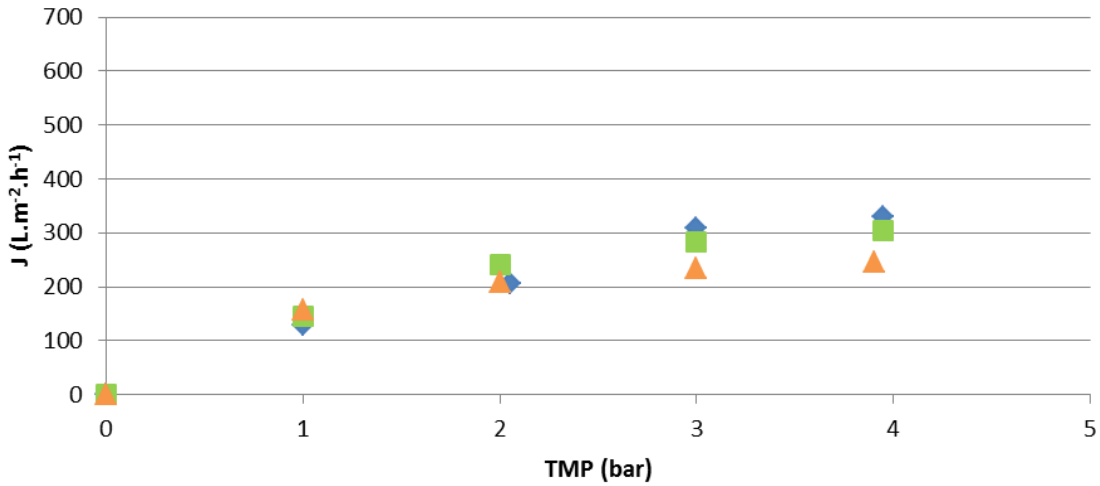
where P_a, P_r and P_p represents the pressure of feed, retentate and permeate, in bar, respectively.

In order to establish their influence, total recycling mode is performed for each experiment which lasted around 20 minutes, times enough for reaching stationary state conditions and then state steady permeation flux is measured.

The variation of permeation flux as a function of TMP for different flow rates (0.6, 0.4 and 0.2 L.min^{-1}) is described in the following figures for both 10 KDa membranes. One membrane is made of cellulose acetate (Figure 14a) and other is made of polyethersulfone, PES (Figure 14b).



(a)



(b)

Figure 14: Permeation flux for different flow rates, 0.6 L.min^{-1} (◆), 0.4 L.min^{-1} (■), 0.2 L.min^{-1} (▲), and transmembrane pressures. (a) Cellulose acetate membrane (b) PES membrane.

Through the figure, it is possible to see an increase in permeation flux with an increase in TMP and flow rate, to achieve, in most cases, a constant value. The formation of this limit can be explained by the formation of a cake layer on the membrane surface that originates the membrane fouling.

The permeation flux of the three flowrate, reaches a practically constant value from a TMP of approximately 2.5 and 3 bar, for the cellulose acetate and PES membrane, respectively. These values of TMP can be considered as an optimum value, because in that range of TMP the tendency to cake layer formation and fouling effect is low. When the constant permeate flux is reached, the membrane fouling by cake layer formation is enhanced so we should not work with a higher transmembrane pressure.

When the recirculation flow rate increases, there is also an increased permeation flux. This can be explained by increased turbulence on the membrane interface. By increasing the flow in consequence there is an increase in the velocity of the fluid, which leads to the removal of some of the accumulated components in the cake layer by hydrodynamic forces, reducing the cake and polarization layer.

The better flow, was about 670 $L.m^{-2}.h^{-1}.bar^{-1}$ for a TMP = 2.7 bar and Qr = 0.6 $L.min^{-1}$, for the cellulose acetate membrane, and about 402 $L.m^{-2}.h^{-1}.bar^{-1}$ for a TMP = 3.3 bar and Qr = 0.6 $L.min^{-1}$, for the PES membrane.

Another very important aspect in the analysis of 10 KDa membrane performances in our case, is that it must allow the passage of polyphenols to the permeate. Given the concentration of polyphenols in the feed to the membrane and in the filtrate, it was possible to determine the percentage of polyphenols retained by the membrane. The percentage of polyphenols retention is defined in according the equation:

$$\%\, retention = \left(1 - \frac{Cp}{Cf}\right) * 100 \qquad 5.3$$

In this equation *Cp* and *Cf* represents the polyphenols concentration, in $mg.L^{-1}$, in the permeate and in feed, respectively.

In Figure 15, it's represent the percentage of retention in versus of transmembrane pressure for each recirculation flowrate. The variation of polyphenol retention is low for both membranes and with the operating conditions. For the cellulose acetate membrane, the retention ranges between 10 % and 20 %. It is difficult to explain the variation of the

retention. However, in the case of the PES membrane, the retention is between 20 % and 30 %. There is a slightly increase with the increasing of the pressure and flowrate.

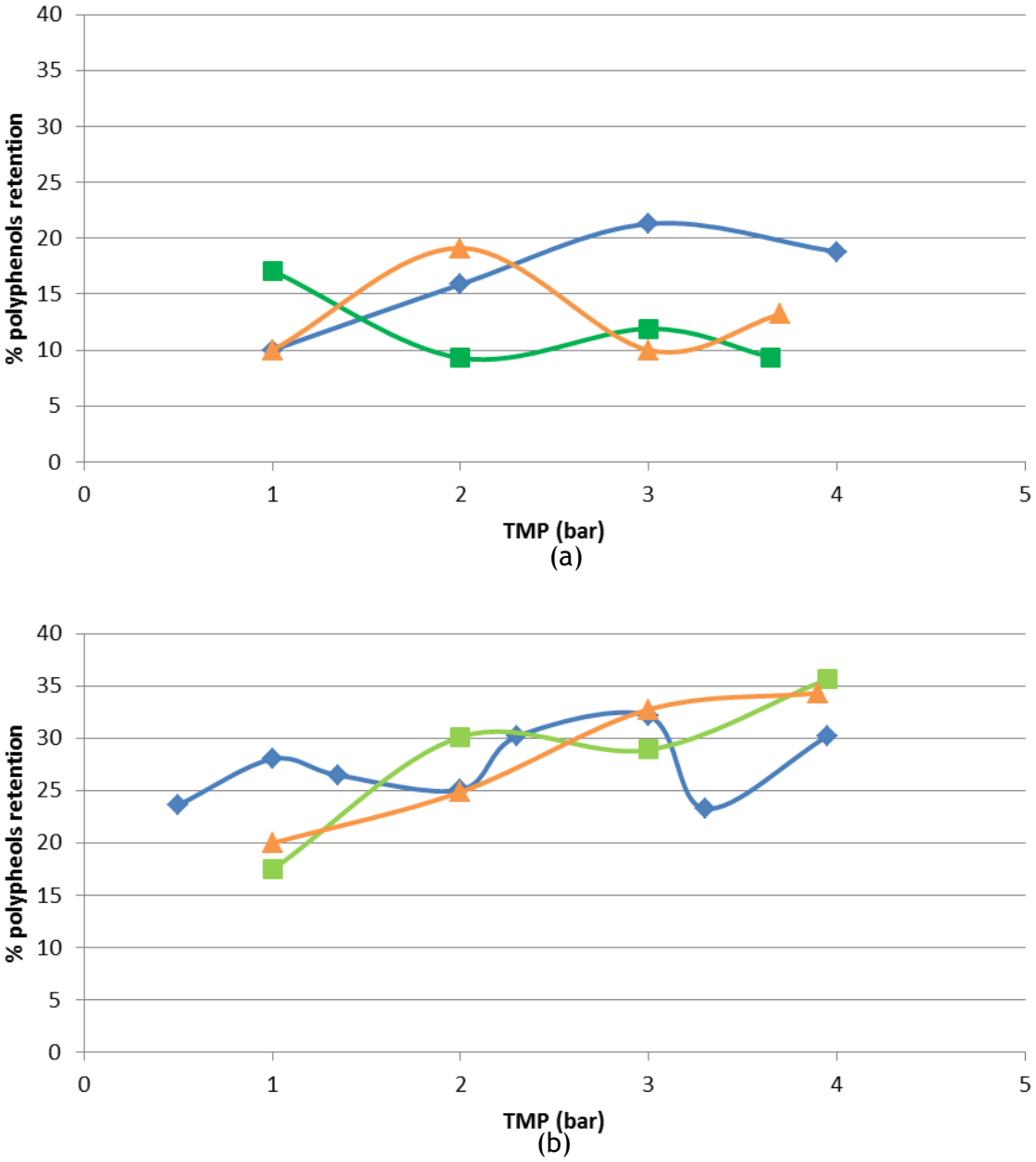


Figure 15: Polyphenols retention rate in function of TPM, and different recirculation flows, 0.6 L.min^{-1} (♦), 0.4 L.min^{-1} (■), 0.2 L.min^{-1} (▲). (a) Cellulose acetate membrane (b) PES membrane.

The difference in the polyphenols retention between both membranes can be explained by their material.

Regarding the permeation flow, both membranes showed results identical to the expected, i.e., in both there was an increase in flux with increasing transmembrane pressure, for different values of the recirculation rate. However, it is evident that the permeation flux is higher with the membrane of cellulose acetate.

Given the retention of polyphenols, it is clear that retention is higher in the PES membrane. However, as we want to recover as much of polyphenols as possible in the permeate, this is a negative aspect for this membrane. Comparing the results of both membranes, it is evident that the membrane which provides the best operating conditions it's the cellulose acetate membrane.

After the comparison was made between the two membranes of higher cut-off, the operating conditions of 1kDa membrane made from PES were optimized. The permeate fluxes with this membrane is much lower than the flux obtained with the 10 kDa membrane, because it has a lower cut-off so it was very difficult to work with low flowrates. With this membrane was used two higher flowrates, 0.8 $L.min^{-1}$ and 0.6 $L.min^{-1}$.

It was the single membrane material proposed by the Pall society.

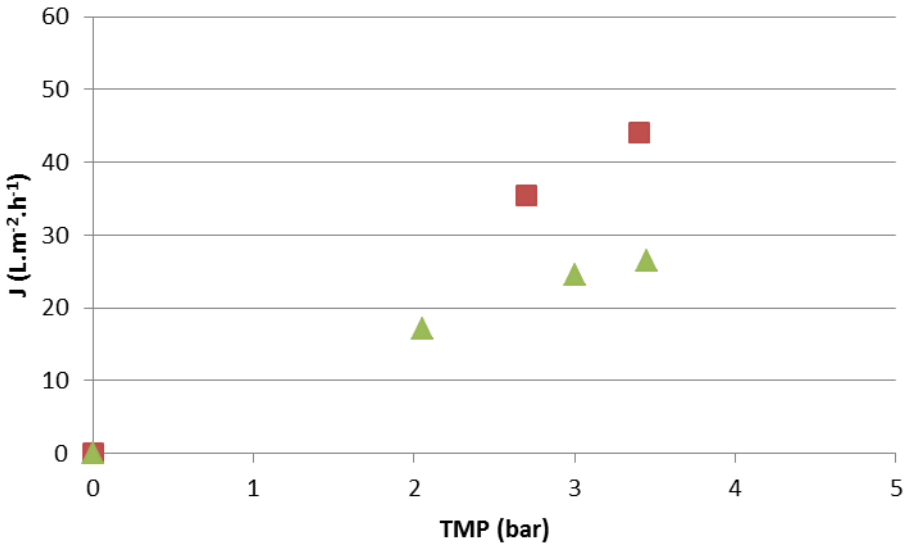


Figure 16: Permeation flux for different flow rates, 0.8 $L.min^{-1}$ (■), 0.6 $L.min^{-1}$ (▲), and transmembrane pressures, with 1 kDa membrane made by PES.

The figure shows a linear increase in the permeation flux when TMP increases without reaching a constant value, indicating that the flow rate does not affect the flow of permeate. The comparison of the permeability (83 $L.m^{-2}.h^{-1}.bar^{-1}$) with the

permeation flux of 17 $L.m^{-2}.h^{-1}.bar^{-1}$ (obtained with TMP = 2 and Qr = 0.6 $L.min^{-1}$) shows a significant decrease of the effluent transfer through the membrane.

Analyzing the retention of polyphenols, the percentage of retention ranges between 40% and 70% .Once again this high retention value can be explained by the interactions between the molecular structure of polyphenols and structure of the membrane material.

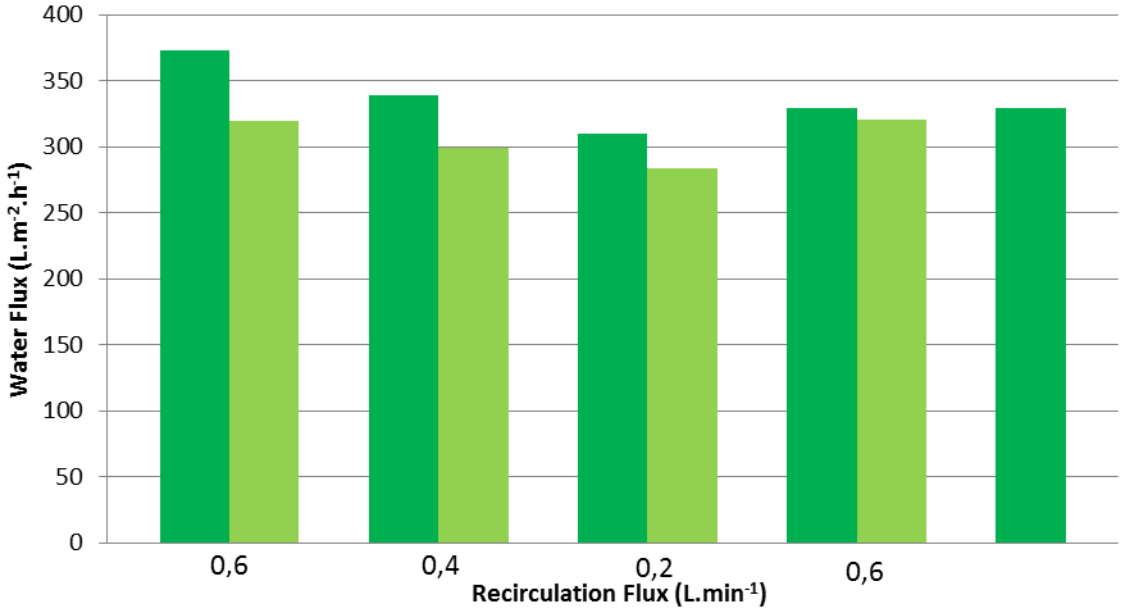
5.2.2 Fouling and cleaning

Flux decline may be caused by membrane fouling which occurs through one or more of the following mechanisms: adsorption and accumulation of solute near the membrane surface (concentration polarization), gradual irreversible changes to the polarized layer and deposition of particles on the membrane. Flux decline can be decomposed into a reversible and an irreversible component. The fraction of the initial water flux which cannot be recovered by a water washing is called irreversible fouling and is related to adsorption or precipitation and/or membrane pore clogging by organic and inorganic compounds

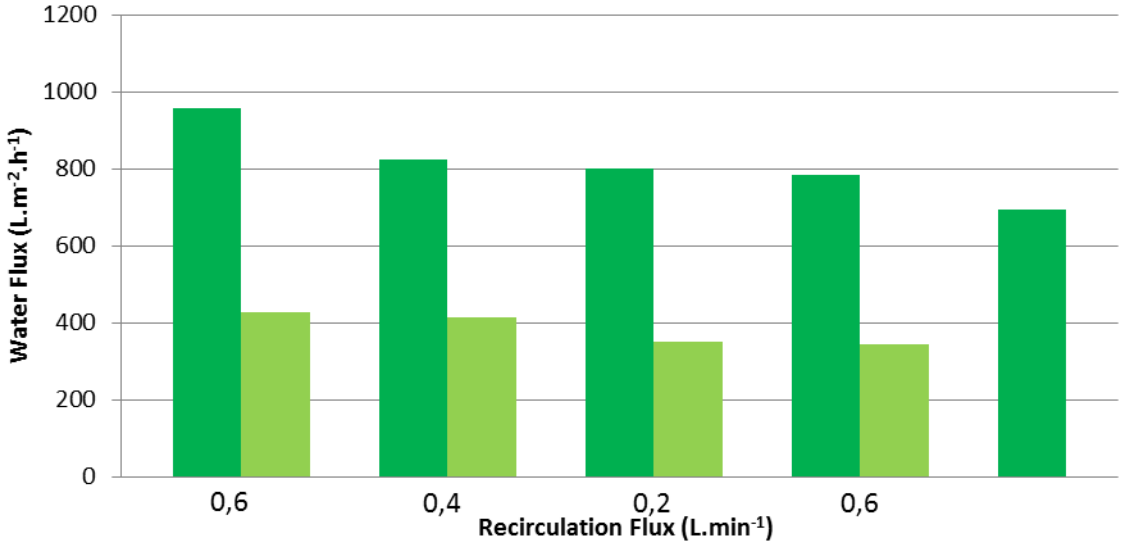
The permeability was measured when the membranes were new and thereafter placed in water until be used again. Before being used, the permeability was verified again.

Every time that the membrane was used with the effluent, it was washed with osmosed water and the water flux was checked, in the same conditions of the permeability. If the water flux decreased, comparing to the initial permeability, the membrane was washed with 0.1M NaOH in circulation on the set up or static with agitation, and permeability was verified again.

In the Figure 17a and Figure 17b, is shown the flow before and after each use, taking into account the flow recirculation used, for the cellulose acetate and PES membranes, respectively.



(a)



(b)

Figure 17: Water flow (a) in PES membrane (b) in cellulose acetate membrane.

As can be seen in the figure, the initial permeability of the PES membrane is much higher than the permeability of the cellulose acetate membrane, although both have the same cut-off. The average permeability of the two membranes with a cutoff of 10 kDa, was 1035 $L.m^{-2}.h^{-1}.bar^{-1}$ and 467 $L.m^{-2}.h^{-1}.bar^{-1}$ to the PES and cellulose acetate membrane, respectively. This may be due to the hydrophilicity of each membrane material. The PES membrane has a high hydrophilicity so wets out quickly and completely, resulting in fast filtration with superior flow rates and high throughputs.

In both figures it is possible to verify a decrease of the water flow with decreasing flow rate recirculation. This fact can be explained by the configuration of the membrane. A lower flow rate causes the particles to deposit at the entrance of the pores, which leads to block

quickly. Other explanation for this phenomenon it's the formation of a thin adsorption layer on the surface of the membrane which made the membrane more hydrophobic. Compounds present in the process water were adsorbed to the membrane surface by the hydrophilic heads and the hydrophobic tails are orientated toward the filtered water [23]. Steryl eters and triglycerides which are the most hydrophobic component of the extractives form the hydrophobic core while fatty and resin acids form the thin surface layer of particles.

However this is reversible in the cellulose acetate membrane, because when the velocity it's increased again, the water flux increased, although continues to be less than the original. At the end of the experimental procedure, the permeability of the cellulose acetate membrane was 329 $L.m^{-2}.h^{-1}.bar^{-1}$, least 30% of the initial permeability. Adsorption tests carried out with this membrane showed that there was adsorption of polyphenols of about 0,007 g, and suspended matter of about 0,1 g.

This phenomenon is not observed in the PES membrane. This fact can maybe be explained by the presence of irreversible fouling, caused by adsorption in the membrane. Adsorption tests made with this membrane show that exists an adsorption of about 0.08 g of polyphenols. Analyzing the figure is easy to verify that the retention of colloidal substances in the PES membrane is far superior since it becomes increasingly difficult to wash this membrane. Every time the PES membrane was used, there was a loss of permeability of about 46%. In the end of the experimental procedure, the permeability of this membrane was 693 $L.m^{-2}.h^{-1}.bar^{-1}$, a loss of permeability around 33%.

The high adsorption in the PES membrane could be related to the hydrogen bonding between hydroxyl group from polyphenol and oxygen atom projecting from SO_2 group in PES (Figure 18).

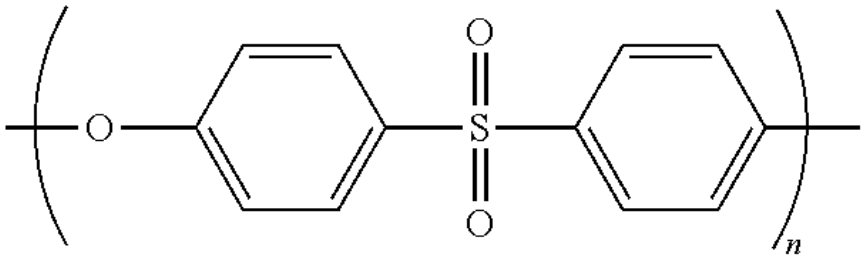


Figure 18: Polyethersulfone (PES)

The benzene ring-benzene ring interaction via π-π stacking is also possible as driving force for the adsorption [24], in both membranes. Also the aromatic part fraction of polyphenols leads to higher aggregating tendency and also facilitates the attachment of polyphenols or polyphenol aggregates to the membrane surface, which is confirmed by the appearance of

brownish yellow color on membrane surface after adsorption test [24], in both membranes but darker in the cellulose acetate membrane, indicating a higher adsorption.

5.2.3 Results of fractionation

After the optimization of operating conditions, the UF set-up was run in the concentration mode for the effluent fractionation. The filtrate does not come back in the reservoir (no recirculation of permeate). The objective is to obtain a molecular fraction with a high concentration of target polyphenols that the molecular weight is between 1000 and 10000 $g.mol^{-1}$.

Analyzing all the results obtained in the optimization of the operating conditions, the following table synthetize the main conditions:

Table 4: Operating Conditions

	Objective	Membrane	Operating conditions
10 KDa	Filtration of target polyphenols	T-Series TFF Cassettes with Omega™ Membrane made by Acetate cellulose	Q_r = 0.6 $L.min^{-1}$ TMP = 2 - 2.5 bar
1 KDa	Retention of target polyphenols Increase the concentration of target polyphenols	T-Series TFF Cassettes with Omega™ Membrane made by PES	Q_r = 0.8 $L.min^{-1}$ TMP = 2 – 3 bar

In this setting, there is placed a specific volume of effluent in the reservoir of the set up. Installation starts with the operating conditions chosen, initially with recirculation of permeate, for about 20 minutes to stabilize the system.

Given that the goal of the first step is to obtain a permeate with a purification of target phenolic compounds, the concentration mode is performed to obtain the maximum possible volume of permeate. In this way there is a reduction of the initial volume which leads to an increase of concentration in the reservoir with time.

Effects of the volume reduction factor (VRF) on flux are shown in the figure. The VRF is defined in according the equation:

$$VRF = \frac{V_f}{V_r} \qquad 5.4$$

where V_f and V_r are the initial volume of the feed and the volume of the retentate, respectively.

In the Figure 19, there is a representation of the evolution of the permeation flux with the volume reduction factor, for three diferent experimets performed on three different days.

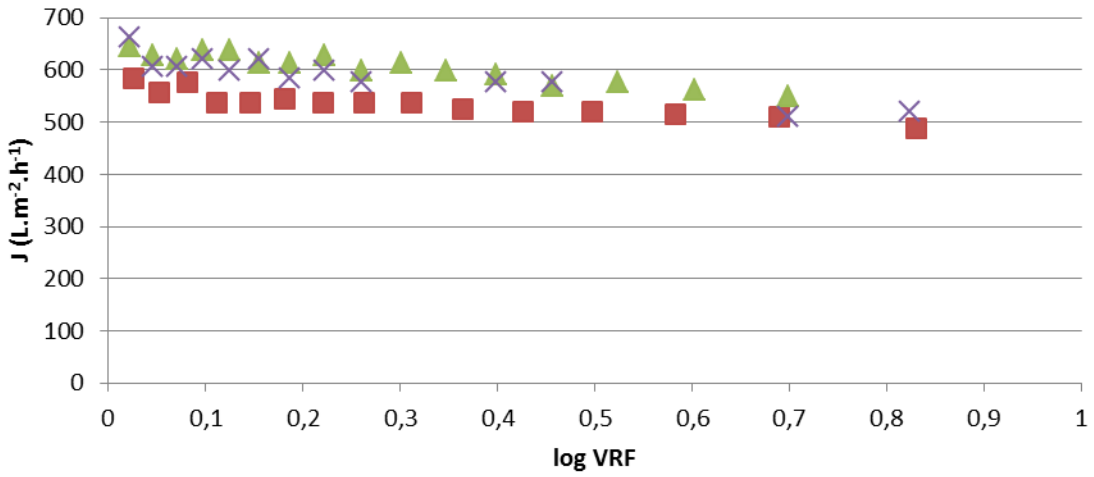


Figure 19: Evolution of the permeation flux with the volume reduction factor. (a) 10 kDa membrane, TMP = 2-2.5 bar and Q_r = 0.6 L.min^{-1}, in three different days: 16/04/2014 (▲). 17/04/2014 (X), 20/05/2014 (■).

In all three experiments the same operating conditions were used, and how it is possible to verify by the figure, the results were very similar. Thus it is possible to say that a good reproducibility was achieved in the experiment.

In the follow figure, it's represented the same results but an average of three experiments was performed and the results are shown for both membranes.

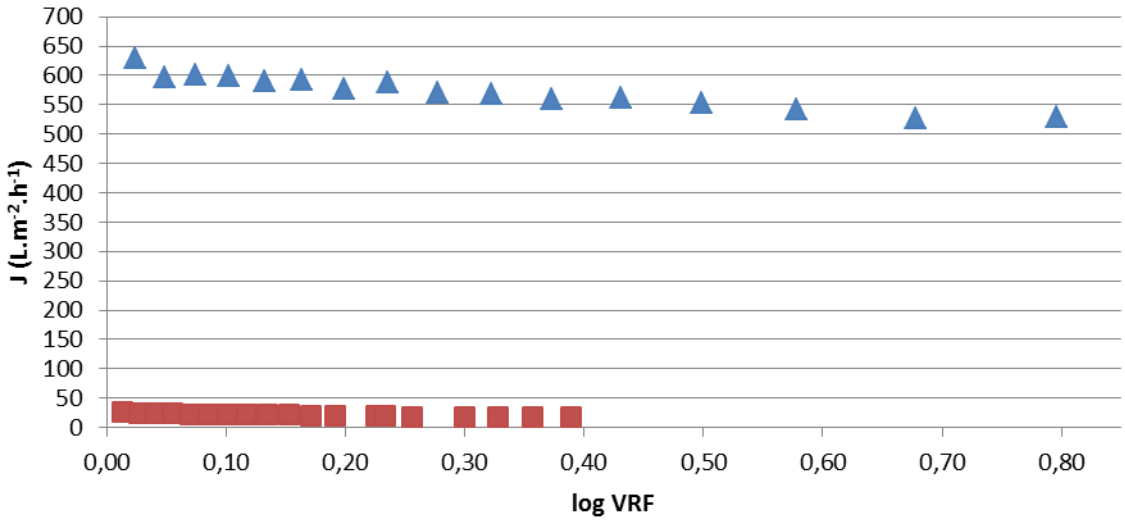


Figure 20: Evolution of the permeation flux with the volume reduction factor. 10 kDa membrane, TMP = 2-2.5 bar and Q_r = 0.6 L.min^{-1}, average of three different days (▲) ;1 kDa membrane, TMP = 2-3 bar and Q_r = 0.8 L.min^{-1}, average of three different days (■).

For both membranes, a very slight decline of permeate flux occurs with the increase in VRF due to increasing fouling effect on the membrane, attributed to the concentration polarization. While the concentration of colloids and particles increases in the concentrate, the thickness of the layer is controlled by hydrodynamic parameter [25].

At the beginning of the process, transmembrane pressure leads to that the particles settling on the membrane surface, which leads to an initial decline in flux. Over time, the recirculation flow leads to provide turbulence near to the cake layer which causes that the particles deposited return again to the effluent in the tank [25]. However, as the concentration in the reservoir increases, the flow continues to decrease but very slowly. This demonstrates that the operating conditions chosen for this process are satisfactory.

The results obtained are similar in both membranes, however the flow in the first kDa membrane flux is much lower than obtained with the 10 kDa membrane. This is due to the fact that the cut-off of the membrane is substantially lower, which makes it more difficult to allow passage the effluent

Having regard to the objective of the fractionation of the effluent, it is important to take into account the variation of the concentration of polyphenols along the process, as well as the percentage of polyphenols retention. In the Figure 21 it's represented the evolution of the concentration of polyphenols, for the 1 kDa membrane, in three different experiments performed in three different days.

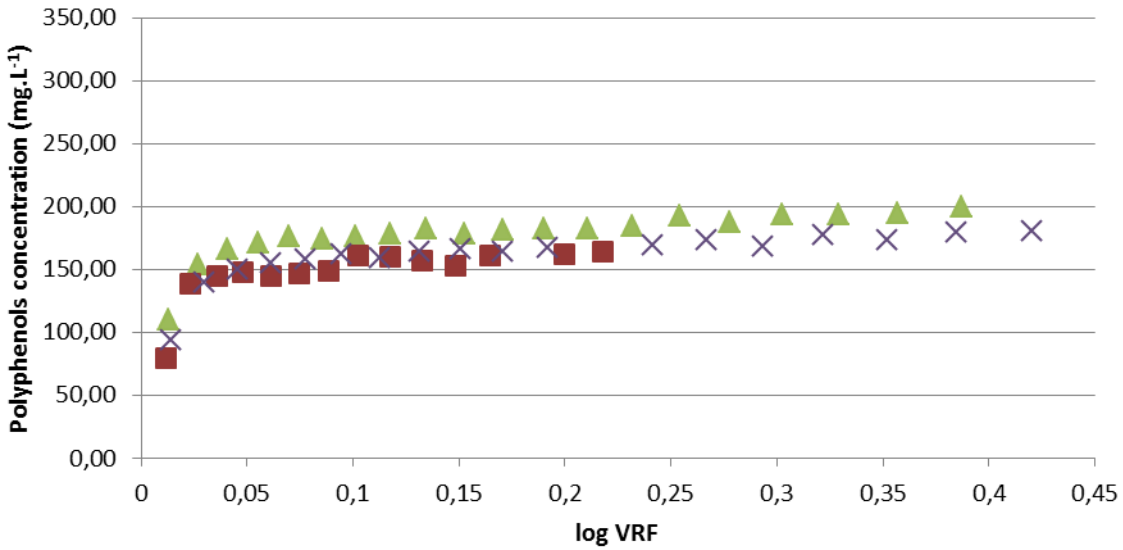


Figure 21: Evolution of the polyphenols concentration with the volume reduction factor. 1 kDa membrane, TMP = 2-3 bar and Q_r = 0.8 L.min^{-1}, in three different days: 12/05/2014 (X), 16/05/2014 (▲), 21/05/2014 (■).

Again it is possible to verify that for the three experiments, the results are similar indicating that was achieved a good reproducibility of the test conditions were obtained.

As expected, the concentration of polyphenols in the permeate slightly increases because with the increasing of volume reduction factor, the concentration in the reservoir will increase.

In Figure 22 it's represented the percentage of polyphenols retention, both in function of the volume reduction factor. For both membranes, was taken the average of three experiments performed in three different days.

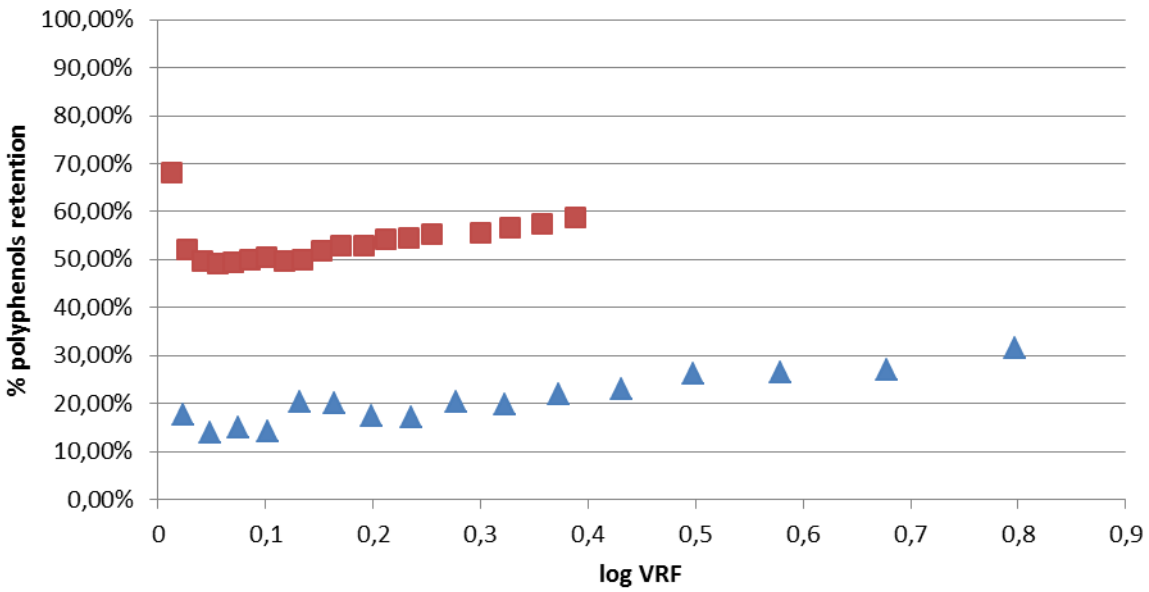


Figure 22: Evolution of the percentage of polyphenols retention with the volume reduction factor. 10 kDa membrane, TMP = 2-2.5 bar and Q_r = 0.6 L.min^{-1}, average of three different days (▲);1 kDa membrane, TMP = 2-3 bar and Q_r = 0.8 L.min^{-1}, average of three different days (■).

The retention of the 1 kDa membrane is clearly higher, with an average retention of 50% whereas for the 10 kDa membrane the retention is about 20%.

In both membranes, it is possible to verify that there is an increase in retention with increase in the volume reduction factor. As explained above, this increase is due to the fact that the concentration in the reservoir increasing as the volume decreases

Given that we obtain a higher permeate volume than what remains in the reservoir is not very correct to make comparison of concentrations between the two streams. Thus it is important that a mass balance was made, for a real evaluation of the process. In the Figure 23, it's represented a schematic representation of the process, with the respective mass balance for each stage of the process.

In the first step, the pre-treatment, one mass balance was not done because the optimal conditions were optimized at the beginning of the study and this step removes a majority of high molecular weight components.

In the second step, ultrafiltration with a 10 kDa membrane was intended to be removed only molecules with molecular weight greater than 10000 g.mol^{-1}, such as hemicelluloses. At this stage it was important that most of polyphenols pass to the permeate. About 72% of the initial amount of polyphenols increased to permeate.

The permeate of the second step was ultrafiltrate with a 1 kDa membrane, and in this stage the aim is to concentrate polyphenols. With this membrane, about 69% of the polyphenols content of the permeate, are retained.

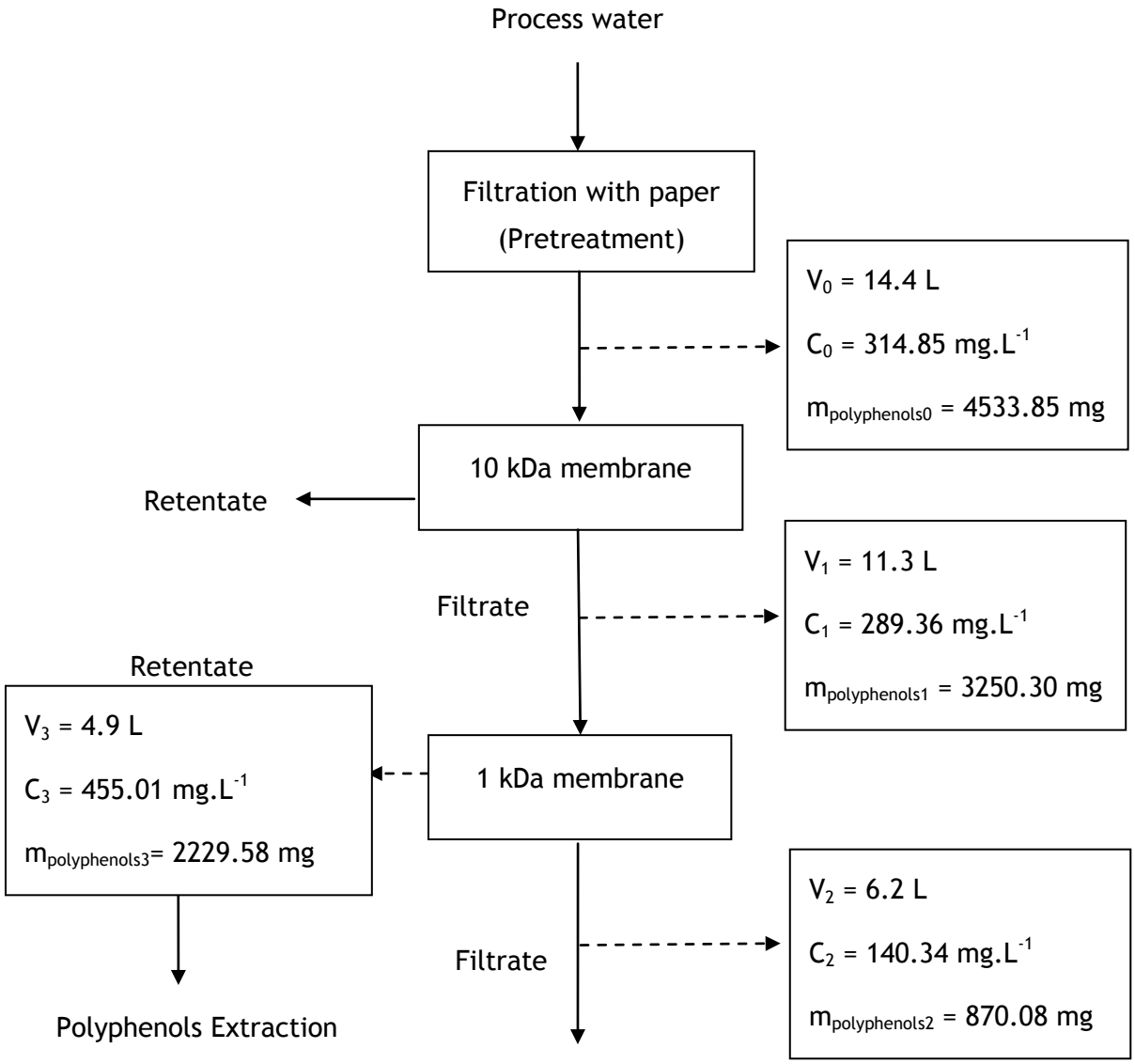


Figure 23: Mass balance about the fractionation

Polyphenols present in this retentate will subsequently be recovered by liquid-liquid extraction, however, by problems of time was not possible to perform this process. This extract will be given to the petroleum refiner in order to evaluate the capacity of this polyphenols fraction to be used as an initiating agent for 'polymerization' and 'condensation' reactions to produce pitch.

6 Conclusions

The main objective of this study was to determine the ability of a pretreatment and an ultrafiltration method for separating polyphenolic molecules from an effluent that comes from a paper industry.

The effluent obtained from a thermo mechanical process was colloidal with a high fouling character and was not suitable for direct UF experiments. Different configurations were used to optimize a filtration with paper, as a pretreatment. The best configuration was two followed filtrations, with different papers, because reduce the colloidal character of the effluent without a high loss of polyphenolic compounds.

To perform the fractionation of the effluent, the best operating conditions were studied with two membranes with same cut-off (10 kDa) but made of different material. The membrane that shows better results was the membrane made of cellulose acetate, at a flow rate of 0.6 $l.min^{-1}$ and a transmembrane pressure between 2 and 2.5 bar. By ultrafiltration with this membrane, was obtained retention of polyphenols of about 20 %.

This permeate was ultrafiltrated with a PES membrane with a cut-off of 1 kDa, and with a recirculation flux of 0.8 l.min-1 and a TMP between 2 and 3 bar. The objective was to get a retentate with a high concentration of polyphenols. With this membrane, there was a retention of polyphenols of about 50%.

The polyphenols extracted from the retentate will be used to evaluate the capacity of this polyphenols fraction to be used in the pitch production.

During this study, was also studied the effect of fouling on the membranes. All of them showed signs of the existence of reversible fouling, like concentration polarization. However, the membranes made by PES showed indications of irreversible fouling, such as adsorption, since cleaning was increasingly difficult where the membrane was used. This can be explained by hydrogen bonding between hydroxyl group from polyphenol and oxygen atom projecting from SO_2 group in PES, and benzene ring-benzene ring interaction via π-π stacking.

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Annex 1 Ultrafiltration membranes and Set Up

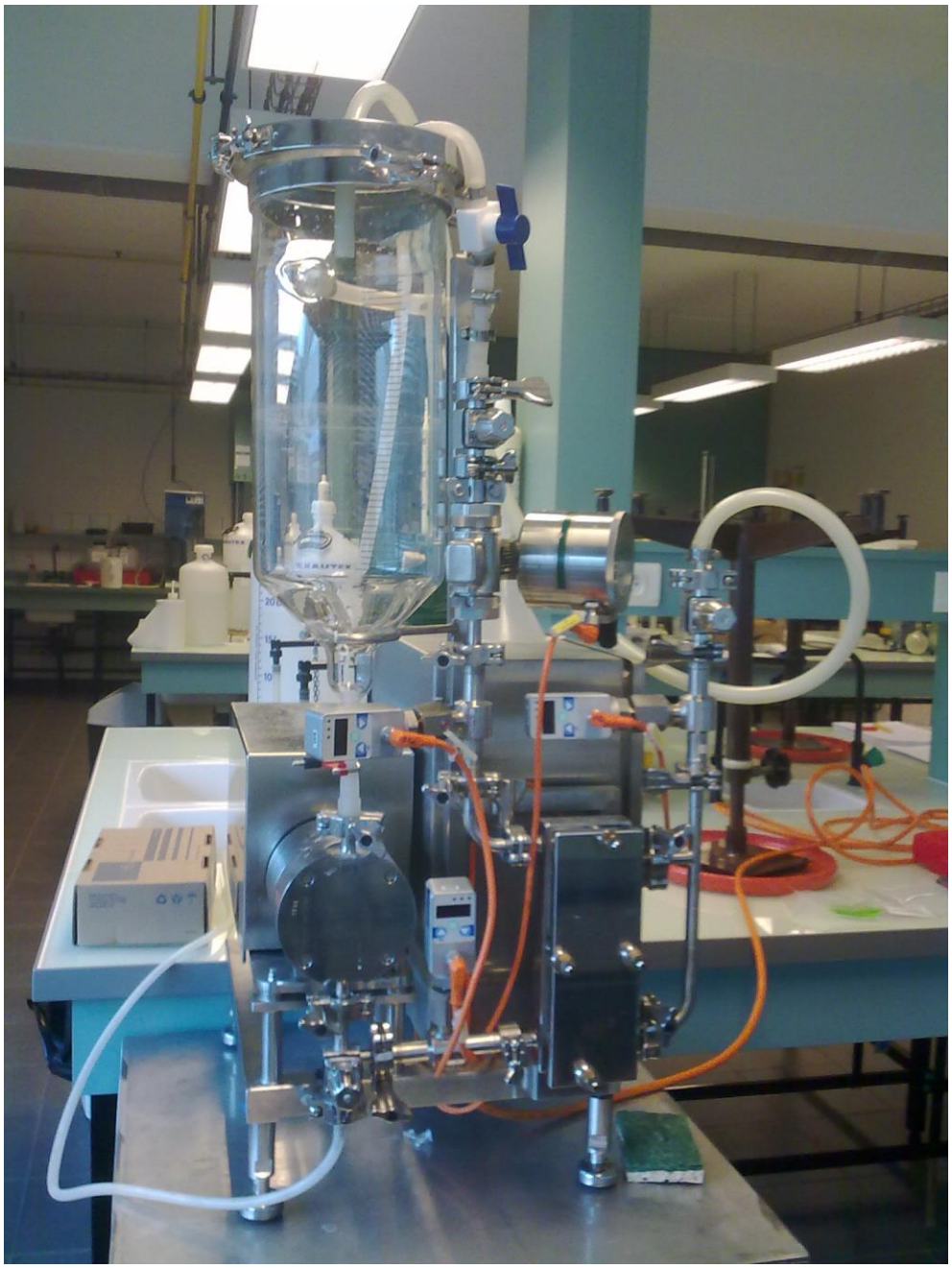

Figure 1: Dispositif d'Ultrafiltration Centramate 500 S Tangential Flow Filtration de la société PALL

Figure 2: Cassettes Centramate™ avec des membranes Omega plane.